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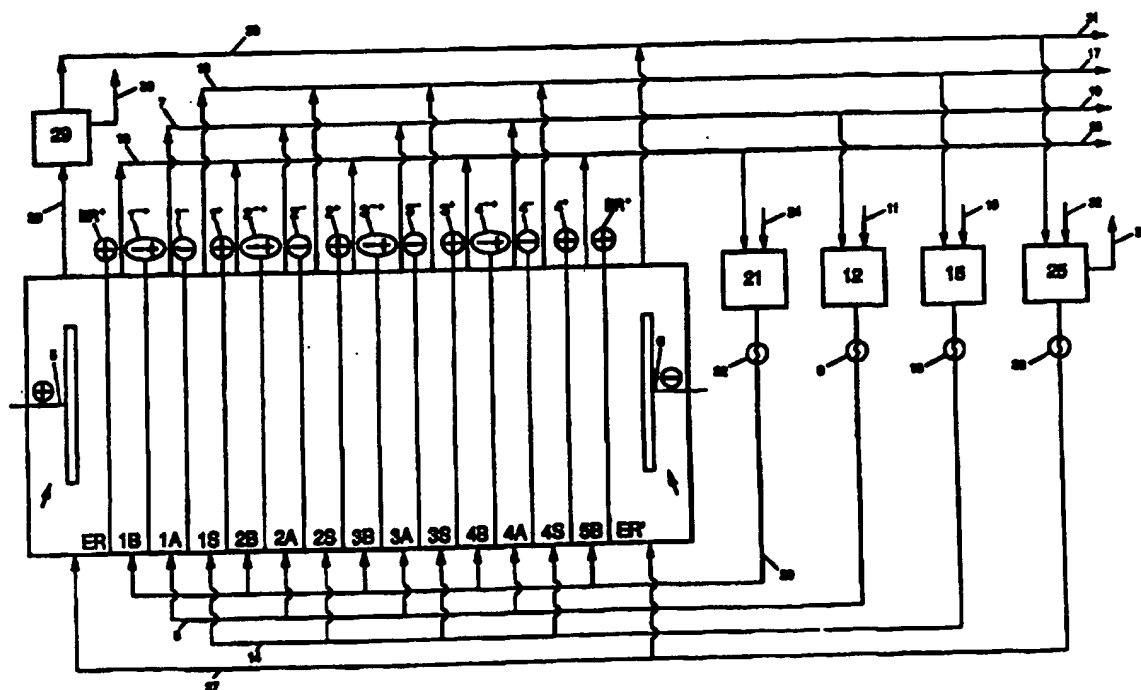
(57) Abstract

Disclosed is a method of making hypophosphorous acid from sodium hypophosphite by performing electrodialytic water splitting upon an aqueous solution of sodium hypophosphite. The process can be tied into an existing process for producing sodium hypophosphite wherein the product of the sodium hypophosphite process is used as a starting material in the hypophosphorous acid process and the depleted sodium hypophosphite solution from the hypophosphorous acid process, which contains some hypophosphorous acid, is used to adjust the pH in the sodium hypophosphite process.

METHOD OF MAKING HYPOPHOSPHOROUS ACID

Background of the Invention

This invention relates to a method of making

5   hypophosphorous acid (HPA) using electrodialytic water

splitting. It also relates to an improved method of making

sodium hypophosphite wherein the sodium hypophosphite is

used in an electrodialytic water splitting process to make

hypophosphorous acid and the depleted sodium hypophosphite

10   from the electrodialytic water splitting process is used to

adjust the pH in the process for making sodium

hypophosphite.

Electrodialytic water splitting is a process in which a

solution of a salt is subjected to a direct current,

15   decomposing water and causing the anions and cations to pass

through anion exchange and cation exchange membranes,

respectively, forming an acid and a base in separate

compartments. For example, if a solution of sodium chloride

is placed between a cation exchange membrane and an anion

20   exchange membrane and is subjected to a direct current,

hydrochloric acid will form on the other side of the anion

exchange membrane and sodium hydroxide will form the other

side of the cation exchange membrane. The concentration of

the acid formed is a function of the current density, but

25   the higher the concentration of the acid, the lower will be

the current efficiency.

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There is also a relationship between the strength of the acid (i.e., how strongly it dissociates to liberate H$^+$) and the concentration of the acid that can be obtained at a particular current efficiency. At the same current

5   efficiency, it is possible to obtain higher concentrations of weak acids than of strong acids. The relationship between the strengths of the acid and the concentration of the acid that can be obtained at a given current efficiency can be found in an article by K. N. Mani titled,

10   "Electrodialysis Water Splitting Technology," Journal of Membrane Science, 58 (1991) pps. 117-138 at page 122. (This article is hereinafter referred to as "Mani, 1991".) In that article it states that at a current efficiency of 80% or higher and a current density of 100 mA/cm^2 the

15   concentration of a strong acid that can be obtained is about 1 normal and the concentration of a weak acid that can be obtained is about 3 to about 6 normal. Because hypophosphorous acid is a strong monobasic acid, the normality and molarity are equal values (i.e., 1N H_3PO_2 = 1M

20   H_3PO_2).

Hypophosphorous acid is now produced by the acidification of sodium hypophosphite. For example, one can load a cation exchange resin with hydrogen ions and pass a solution of sodium hypophosphite over the resin so that the

25   sodium ion is exchanged for the hydrogen ion and hypophosphorous acid is produced. Until now, the production of hypophosphorous acid by electrodialytic water splitting has not been suggested or attempted. One possible reason

for this is that the readily available references for HPA
describe it as a strong acid. As a strong acid, the
concentration of HPA that could be produced at a given
current efficiency would be low, requiring a choice between

5   high power consumption to make a high concentration of acid
and high energy consumption to evaporate water from a low
concentration of acid. Van Wazer, Phosphorus and Its
Compounds, Vol I., page 359 (1958), the definitive reference
on phosphorous chemistry, describes HPA as a strong

10   monobasic acid with a dissociation constant of 8.0 X 10^{-2}
(pKa = 1.1). On the other hand, K. Mani in WO 92/11080
defines a weak acid for the purpose of electrodialytic water
splitting as one with a pKa of 3 or greater, but generally
less than 11. The electrodialytic water splitting of sodium

15   hypophosphite would therefore be expected to produce
hypophosphorous acid having a concentration of about 1
normal at a current efficiency of 80%. Another reason,
relating to production in conventional electrolytic membrane
cells, may be due to product quality concerns associated

20   with oxidation of the hypophosphorous acid at the anode to
produce phosphite anion contamination of the product.

                    Summary of the Invention
         We have discovered that when hypophosphorous acid is

25   produced by the electrodialytic water splitting of sodium
hypophosphite at 80% current efficiency, the concentration
of the hypophosphorous acid produced is not the 1 normal
concentration that would be expected for a strong acid, but

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instead is about 2.2 normal. While we are unable to account

for the unusually high concentration of hypophosphorous acid

that can be obtained, the result is very beneficial because

it reduces the amount of evaporation that is needed to

5   produce high concentrations of the acid. As a result, the

production of hypophosphorous acid by electrodialytic water

splitting may be competitive with other methods of producing

that acid.

We have also discovered that the production of

10   hypophosphorous acid by electrodialytic water splitting can

be tied into an existing process for producing sodium

hypophosphite. That is, the sodium hypophosphite product

from an existing process can be used as the starting

material in the electrodialytic water splitting process and

15   the depleted sodium hypophosphite salt from the

electrodialytic water splitting process, which contains some

hypophosphorous acid, can be used to adjust the pH in the

existing sodium hypophosphite process. When this is done,

the existing sodium hypophosphite process is improved in

20   several ways. The product value of the hypophosphorous acid

in the depleted salt stream is recovered instead of being

neutralized with the dilute caustic stream prior to

resaturation with sodium hypophosphite crystal. This not

only allows product acid, which would otherwise be lost to

25   be effectively utilized in the process, but also allows more

of the weak caustic product solution to be utilized as feed

in the sodium hypophosphite process. The use of acids other

than hypophosphorous acid in the existing sodium

hypophosphite process to adjust the pH is eliminated, and therefore the sodium hypophosphite product will contain hypophosphite instead of foreign anions and be purer. This will also reduce the amount of calcium salt waste material

5   that is generated, which has a significant disposal cost. Also, the calcium salt waste material is thixotropic, which means that it releases water when it is shaken, and since it must be disposed of as a solid waste, this is unacceptable for companies that accept solid waste for disposal. The

10   substitution of hypophosphorous acid for other acids in the existing sodium hypophosphite process unexpectedly eliminates this problem.

In addition, the dilute caustic generated in the electrodialytic water splitting process can be incorporated

15   into the sodium hypophosphite process without penalty as a source of NaOH in the phosphorous hydrolysis portion of the process. The dilute caustic can also be used to generate calcium hydroxide from lime needed in the sodium hypophosphite process.

20   While there are a number of ways of tying together the electrodialytic water splitting process for producing hypophosphorous acid with existing processes for producing sodium hypophosphite, in one method the mother liquor from an existing sodium hypophosphite process, which contains

25   both sodium hypophosphite and sodium phosphite, could be used in the electrodialytic water splitting process. This eliminates the need to purify the liquor and evaporate water from it. Although this liquor contains both phosphite ion

and hypophosphite ion, it is believed that the two ions can

be at least partially separated in the electrodialytic water

splitting process because the hypophosphite ion is smaller

than the phosphite ion and can therefore pass more easily

5   through the anion exchange membrane. European Patent

Application 0459751A1 also teaches that adjustment of the

depleted salt feed to alkaline conditions will improve the

separation by forcing the phosphorous anion to become

divalent.

10   The electrodialytic water splitting process for

producing hypophosphorous acid can also be tied into the

existing ion exchange process for producing hypophosphorous

acid. That is, instead of using the ion exchange process to

produce all the hypophosphorous acid from sodium

15   hypophosphite, it could instead be used to exchange hydrogen

ions for the small concentration of sodium ions in the

hypophosphorous acid produced by the electrodialytic water

splitting process of this invention. This would lower the

overall cost of producing hypophosphorous acid of high

20   purity.

Brief Description of the Drawings

Figure 1 is a diagrammatic side view which illustrates

an electrodialytic water splitting process according to this

25   invention for producing hypophosphorous acid.

Figure 2 is a block diagram which illustrates an existing process for producing sodium hypophosphite and shows how the electrodialytic water splitting process for producing hypophosphorous acid according to this invention ties into that existing process.

Figure 3 is a graph giving the results of Examples 3, 4, and 5. In Figure 3 the ordinate is current efficiency and the abscissa is normality (Eq/L).

Description of the Invention

Figure 1 shows an electrolytic cell according to this invention. The cell is formed from four juxtaposed units, 1, 2, 3, and 4. Each unit has an acid compartment, 1A, 2A, 3A, and 4A, a salt compartment, 1S, 2S, 3S, and 4S and a base compartment, 1B, 2B, 3B, and 4B. The anode 5 is in the anode side electrode rinse (ER) acid compartment and the cathode 6 is in the base side electrode rinse (ER') compartment. Separating the acid and salt compartments of each unit are anion exchange membranes 1^-, 2^-, 3^-, and 4^- and separating the salt and base compartments are cation exchange membranes 1^+, 2^+, 3^+, and 4^+. Beginning each unit is a bipolar membrane 1^{-+}, 2^{-+}, 3^{-+}, and 4^{-+}. The two electrode rinse membranes, ER^+, separate the beginning and ending of the unit cells from the electrode compartments and generally consist of commercially available Nafion® type membranes. The rinse compartments which are fed dilute caustic are segregated from the unit cells in hypophosphorous acid production because the oxidizing

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environment of the anode compartment could oxidize the
reducing acid, generating phosphites which would
detrimentally impact product quality. For this reason, the
use of electrodialytic water splitting technology represents
5   a distinct improvement over conventional electrolysis and is
probably the reason why electrolytic production of HPA has
not been reported in the open literature. (Cationic
exchange membranes and anionic exchange membranes are
commercially available. Bipolar membranes are manufactured
10   by Aquatech Systems, a Division of Allied-Signal, and are
described in U.S. Patents Nos. 2,829,095; 4,116,889;
4,024,043; and 4,082,835; herein incorporated by reference.)

The compartments are sealed by means of gaskets (not
shown) and the fluids in the compartments are recirculated
15   to prevent the build-up of ions near the membranes. The
fluid in acid compartments 1A, 2A, 3A, and 4A is
recirculated through lines 7 and 8 by means of pump 9.
Hypophosphorous acid product is removed through line 10 and
additional water is added through line 11. The capacity of
20   the recirculating system is increased by means of storage
tank 12. Similarly, fluid in salt compartments 1S, 2S, 3S,
and 4S is recirculated through lines 13 and 14 and storage
tank 15 by means of pump 16. Depleted salt solution is
removed through line 17 and additional fresh salt solution
25   is added through line 18. Fluid in base compartments 1B,
2B, 3B, 4B, and 5B is recirculated through lines 19 and 20
and storage tank 21 by means of pump 22 and sodium hydroxide
is removed through line 23 while fresh water is added

through line 24. Finally, the electrode rinse solution in compartments ER and ER' is recirculated through lines 27, 28, and 30 and storage tanks 25 and 29 by means of pump 26. A purge, if required, can be removed through line 31 while fresh make-up solution can be added through line 32. Oxygen and hydrogen formed in the electrode rinse compartments, ER and ER' disengage in vessels 29 and 25 and exit through lines 33 and 34, respectively. The removal of product solution from the respective recirculation loops can be accomplished at any point in the loop as long as the pressure differential between compartments is not influenced by the removal process.

The production of gaseous hydrogen 34, and oxygen 33, occurs only at the anode and cathode. Since the production of these gases increases energy consumption per unit of product, it is advantageous to juxtapose a large number of units using common bipolar membranes in between them to minimize the production of these gases relative to the product streams. However, if the number of units in the cell is too large, power consumption again begins to increase and the total voltage across the stack becomes excessive. While the drawing illustrates only four units, any number of units can be similarly juxtaposed and a typical cell may contain about one to about two hundred units.

To operate the cell, it is assembled and HPA and weak NaOH solutions are circulated through the respective acid and base compartments while an aqueous solution of sodium

hypophosphite and HPA is circulated through the salt

compartment. A weak solution of caustic is also circulated

through the electrode rinse compartments. The salt

compartment contains both sodium hypophosphite and HPA

5   because of the inequality between the acid and base current

efficiencies. When the base current efficiency is greater

than the acid current efficiency, the salt compartment

contains sodium hypophosphite and HPA. When the acid

current efficiency is greater than the base current

10   efficiency, the salt compartment contains sodium

hypophosphite and NaOH. Under most conditions, the base

conductivity will be greater than the acid conductivity.

The concentration of sodium hypophosphite in the salt loop

that is used can vary from about 1 wt% (based on solution

15   weight) up to saturation (about 55 wt%), but it is

preferably about 5 to about 30 wt% because at less than

about 5 wt% the solution conductivity drops to a point where

cell voltage and heat generation associated with the

increased ohmic drop make the operation of the cell

20   difficult, and at over about 55 wt% there is a risk that

sodium hypophosphite may precipitate in the membranes. The

HPA concentration in the salt loop can vary from 0 wt% to

the same concentration as the acid compartment (a maximum of

about 55 wt%). The cell can be operated at temperatures

25   between 10°C and about 50°C, but it is preferable to operate

at about 25 to about 40°C as the cell generates heat and

cooling requirements are reduced by operating above room

temperature. No pH adjustments are normally required to

operate the cell. The current density used is preferably about 50 to about 155 mA/cm^2 and the cell voltage can vary from about 1.6 to about 2.5 volts/unit, depending on cell geometry, its operation and current density, but is

5   typically about 1.8 to about 2.0 V/unit, direct current (DC). While recirculation of the fluids is required to prevent damage to the membranes, the rate can vary widely although about 5 to about 15 cm/sec is recommended. The overall reaction in the cell is:

10              $$NaH_2PO_2 + H_2O \longrightarrow NaOH + H_3PO_2.$$

There are a number of ways of operating the cell. In the batch mode, most or part of the fluid in the recirculation system of the acid compartment is removed as product and is partially replaced by fresh water whenever

15   the acid concentration reaches a certain predetermined value. For example, when the hypophosphorous acid concentration reaches a predetermined concentration between 5 and 55 wt% sufficient acid can be removed and replaced with water to reduce the acid concentration to the lower

20   limit. Preferably, this is done when the acid concentration reaches a predetermined concentration between about 10 and about 30 wt%. The base and salt loops can be operated in a similar fashion and combinations of batch and continuous processes for the product and feed streams can also be

25   employed.

In the continuous mode of operating the system, acid product is continuously removed and replaced with fresh water to maintain the hypophosphorous acid concentration at

a certain predetermined concentration. The concentration of the acid is maximized when there is no water addition to the cell at a given set of operating conditions. While the batch mode of operation is more energy efficient, it

5   requires more careful monitoring of the system and more controls in the system than does the continuous mode.
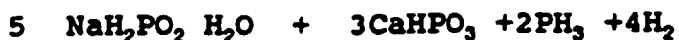
In both modes it is advantageous to keep the sodium hypophosphite salt concentration feed to the recirculation loop at a uniform level and preferably between 5 and

10   saturation (about 55 wt%). It is also preferable to keep the sodium hydroxide concentration low to prevent sodium ions from migrating from the base compartment into the acid compartment through the bipolar membrane, which would reduce the concentration of acid and contaminate the remaining acid

15   with salt. A concentration of sodium hydroxide between about 1 and about 20 wt% is recommended and it is preferable to keep the sodium hydroxide concentration below about 5 wt%. In order to maximize product quality, the hydrodynamic head of the HPA recirculating loop should be 1 to 2 psi

20   higher than the salt or base recirculating loops. The higher pressure discourages mass transport of NaOH and sodium hypophosphite into the acid compartment. If a pinhole develops in a membrane, operating at higher differential pressures will minimize HPA contamination.

25   Keeping the sodium hydroxide concentration low increases the acidity of the spent salt solution, which is advantageous if the spent salt solution is to be used for pH adjustment in the existing process for producing sodium

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hypophosphite. For that purpose, a pH of about 1.5 to about
4 for the depleted salt solution is desirable. Also, if
the acid content of the spent salt solution is to be used
for pH control in the existing process for producing sodium

5   hypophosphite, the concentration of acid and base in the
acid compartment and base compartment, respectively, can be
controlled so that the acid content of the spent salt
solution is appropriate for that purpose (i.e., so that at
least no additional acid is needed in the sodium

10   hypophosphite process to adjust the pH).

The concentration of the hypophosphorous acid in the
acid compartment can be increased up to about 55 wt%, but
the current efficiency falls off as the concentration
increases and the concentration of sodium in the product

15   acid increases. A current efficiency of 80% at a
concentration of 2.23 normal hypophosphorous acid (14.3 wt%)
can be achieved. This is unusually high, a little more than
double what the teachings of the prior art would lead one to
expect.

20   Figure 2 illustrates an existing process for producing
sodium hypophosphite and shows how the electrodialytic water
splitting process of Figure 1 ties into that process.
Calcium hydroxide, produced in mixing vessel 35 is made by
mixing water from line 36 with lime (CaO) from line 37. The

25   calcium hydroxide passes through line 38 to reactor 39 where
it is mixed with phosphorus-containing water from line 40
and elemental phosphorus from line 41 along with sodium
hydroxide from line 42. The reaction:

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$$5 \text{ NaOH} + 2.5 \text{ } P_4 + 3Ca(OH)_2 + 13 \text{ } H_2O \longrightarrow$$

$$5 \text{ } NaH_2PO_2 \text{ } H_2O + 3CaHPO_3 + 2PH_3 + 4H_2$$

is believed to occur in reactor 39. Phosphine and hydrogen

gases are removed from reactor 39 through line 43. The

5   products, a slurry of precipitated calcium phosphite and

dissolved calcium hypophosphite in sodium hypophosphite

solution, pass through line 44. They are combined with

mother liquor from solid/liquid separator 45 from line 46

and are fed to solid/liquid separator 47, where the

10   precipitated calcium phosphite is removed through line 48.

The solution of sodium and calcium hypophosphite passes

through line 49 to calcium precipitator 50 where sodium

carbonate in line 51 is added to precipitate calcium

carbonate. The slurry passes through line 53 to calcium

15   carbonate solid/liquid separator 54 where the calcium

carbonate is removed through line 55. The liquor of sodium

hypophosphite passes through line 56 where, in the existing

process, an acid is added through line 57 to lower the pH

and precipitate sodium hypophosphite in

20   evaporator/crystallizer 58. The slurry passes through line

59 to solid/liquid separator 45 which separates the mother

liquor in line 46 from crystalline sodium hypophosphite.

The crystalline hypophosphite in line 60 is dried in dryer

61 and forms the product in line 62. The mother liquor in

25   line 46 is recycled and combined with line 44 which feeds

the solid/liquid separator 47. Further details on existing

processes for producing sodium hypophosphite which can be

combined with the process of this invention for producing

hypophosphorous acid can be found in U.S. Patents Nos.
3,052,519; 2,976,117; 4,521,391; 4,380,531; and EP 459751A1,
herein incorporated by reference.

If crystalline sodium hypophosphite is used in the
hypophosphorous acid process, it is dissolved in tank 63,
then passed through line 64 to cation exchange material 65,
which removes any divalent (e.g., calcium and magnesium)
ions that may be present as these may damage the ion-
exchange membranes. (Depending on the purity of the product
formed in the sodium hypophosphite process, ion exchange
material 65 may be unnecessary.) The purified sodium
hypophosphite passes through line 66 into the salt
compartment (and through its recirculation system) of
electrolytic cell 67. Water is added to the cell from line
68 and sodium hydroxide produced in the process is removed
through line 69 where it is sent to vessel 35 or to reactor
39 (dotted line 70) or to the calcium precipitator 50
(dotted line 71). When the sodium hydroxide or a portion
thereof is sent to vessel 50 through dotted line 71, CO_2 is
added through dotted line 52 in order to generate carbonate
in situ. The sodium carbonate entering through line 51 can
then be reduced nearly stoichiometrically.

Depleted salt from the hypophosphorous acid process can
be recycled through line 72 to crystallizer/evaporator 58.
If this is done, it is not necessary to add an acid from
line 57 to the sodium hypophosphite liquor. A portion of
the depleted salt can be recycled to dissolving tank 63
through line 73. Hypophosphorous acid, which is typically

about 10 to about 50 wt%, is removed through line 74. It can be taken as a product from line 75 or it can be sent to evaporator 76 and concentrated to about 25 to about 70 wt% and taken as a concentrated product from line 77.

5   The sodium hypophosphite used in the hypophosphorous acid process can be obtained from various locations in the sodium hypophosphite process. If sodium hypophosphite crystals are used they can be obtained from solid/liquid separator 45 through line 78 or from the product drier

10   through line 79. Alternatively, sodium hypophosphite liquor in line 56 or mother liquor in line 46 can be sent through lines 80 or 81, respectively, to ion exchange bed 65.

The following examples further illustrate this invention.

15

Example 1

A bed volume (BV) of 22 cm^3 of Dowex G-24 ion exchange (IX) resin was placed in a column. The IX resin bed had a length to diameter ratio of 6.8. Hypophosphorous acid (15.0

20   wt%) with 1522 ppm Na was pumped from a reservoir to the top of the bed. The solution was fed at a rate of 0.144 BV/min. Samples were collected as a function of time and related to the total number of BV which had passed through the column. The ppm Na was measured using a sodium ion selective

25   electrode and the wt% H_3PO_2 was measured by NaOH neutralization to pH 7. The data were collected and are:

30

#BV	ppm Na	wt% H_3PO_2
1.1	12.2	2.8
3.2	5.8	14.0
5.4	32	15.4
7.5	219	15.4
9.6	571	15.3
11.7	1185	15.2
13.9	1194	15.1
16.1	1509	15.1
18.2	1537	15.2
20.3	1565	15.0
22.5	1560	15.1

The experiment was stopped because the IX resin was
saturated with Na^+. Approximately 420 ml of deionized water
was used to backwash the IX bed and to remove residual
H_3PO_2. Then, 190 grams of 10 wt% HCl was used to regenerate
the resin, which was subsequently backwashed with
approximately 190 ml of deionized water. The column was
placed in service again.

Based upon the amount of sodium removed by the IX
resin, the capacity was estimated to be 0.61 meq/ml of
resin. The reported capacity is 2 meq/ml of resin.
Therefore, the resin $[H^+]/[Na^+]$ ratio is (2-0.61)/0.61 =
2.27, indicating a much better Na^+ selectivity than expected
from the literature (e.g., 3.65).

Example 2

Hypophosphorous acid 14.9 wt% with 1540 ppm Na was pumped from a reservoir to the top of the regenerated bed used in Example 1. The solution was fed at a rate of 0.149 BV/min. Samples were collected and analysis performed in an identical manner as given in Example 1.

#BV	ppm Na	wt% H_3PO_2
1.3	57	5.7
3.5	63	14.1
5.7	88	15.0
7.9	288	15.1
10.1	810	15.1
12.4	1121	14.9
14.6	1461	15.0
16.8	1309	17.9
19.1	1542	14.9
21.3	1535	14.9
23.6	1537	14.8

This example shows that the column can be regenerated and be used to remove sodium from hypophosphorous acid.

Based upon the amount of sodium removed by the IX resin, the capacity was estimated to be 0.66 meq/ml of resin. The reported capacity is 2 meq/ml of resin. Therefore, the resin $[H^+]/[Na^+]$ ratio is (2-0.66)/0.66 = 2.03, indicating a much better Na^+ selectivity than expected from the literature (e.g., 3.65).

Cell Examples

In the following examples, a laboratory cell setup was utilized which was similar to those described in WO 92/11080. A laboratory cell which is configured as shown in Figure 1, was used to accomplish the splitting of sodium hypophosphite into hypophosphorous acid and sodium hydroxide utilizing a combination of anion, cation, and bipolar ion exchange membranes. The cell consisted of two end blocks which were fabricated to form the respective anode and cathode electrode rinse compartments for the cell. The ion exchange membranes, separated one from the other with gaskets, formed the individual acid, base, and salt compartments. The thickness of the gaskets was 50 mils, and the gaskets were cut so as to create an open area of 3.6 square inches central to the gasket to allow solution flow through the exposed faces of the membranes. As an aid to solution distribution across the face of the membranes, expanded plastic mesh was set into the compartment formed by the open area of the gasket and bounded by adjacent membranes. The gaskets were manifolded at the bottom and top of each compartment to create channels of flow for the acid, base, and depleted salt solution entering and exiting the cell stack and to prevent cross contamination of the solutions between the flow channels.

The order of the membrane types, starting from the anode end block, consisted of a cation membrane followed by four sets of three membranes which repeated the pattern bipolar, anion, and cation. The bipolar membranes were

oriented so that the anion side always faced the anode. An additional cation exchange membrane followed just ahead of the cathode compartment. Thus, there were a total of 15 compartments consisting of 2 electrode rinse compartments, 5 base compartments, 4 acid compartments, and 4 salt compartments. The anode and cathode compartments were fed an electrode rinse solution which carried gas generated at the electrodes out of the cell, where it separated from the solution in the recirculation reservoir and was vented.

Nafion® 324 was used as the cation exchange membrane forming the electrode rinse compartments. The bipolar membranes were prepared according to U.S. Patent 4,766,161. The cation exchange membranes were prepared according to U.S. Patent 4,738,764. The anion exchange membranes were from Asahi Glass Co. (sold under the tradename Selemion® AMV anion permselective membranes). The cell was equipped with a nickel anode and a stainless steel cathode.

Four pumps were used to circulate the acid, base, depleted salt, and the combined electrode rinse solutions in and out of the cell and through calibrated recirculation vessels. These pumps were operated in a such a way so that the linear velocity of the solution in the cell was maintained at about 15 cm/sec. This allowed each cell stream to be operated independently in one of two different modes - batch/semi-batch and continuous.

The cell was powered by a DC constant current rectifier capable of providing 20 amps of current at up to 50 V. A

current density of 100 amps per square foot was maintained
in all examples. The temperature in the cell was maintained
at 35°C.

A 10 wt% NaOH solution was used for the electrode rinse

5   solution. The anode and cathode electrode rinse solutions
exiting the cell were continuously recombined into a common
recirculation tank. The acid and base compartments were
initially inventoried with hypophosphorous acid and 5% NaOH.

A 25 wt% sodium hypophosphite solution with a calcium

10   concentration of less than 1 ppm was used to replenish the
depleted salt stream and maintain a constant solution
conductivity. The 25 wt% salt solution was prepared by
dissolving 25 g of technical grade sodium hypophosphite
monohydrate crystal in 75 g of DI water per 100 g of feed

15   solution. The pH of this solution was 7.2. The salt
solution was adjusted with caustic in order to raise its pH
to 10 and thus facilitate calcium removal via a Duolite C467
ion exchange resin. Ion exchange was accomplished by
passing the salt solution through a column packed with the

20   Duolite resin, which is manufactured by Rohm & Haas. The
initial Ca concentration of the 25 wt% solution was measured
by Inductively Coupled Argon Plasma (ICP) to be 8 ppm and
that of the final solution <1 ppm.

25   Example 3

This example shows that higher hypophosphorous acid
concentrations are obtained at a given current efficiency
relative to those reported for other strong acids produced

during the electrodialytic splitting of sodium hypophosphite
salt into its acid and base components using a three-
compartment cell equipped with anion, cation, and bipolar
membranes.

5   In this test, the salt and base streams were operated
in a continuous bleed and feed mode. The base loop caustic
concentration was maintained at about 5 wt% NaOH with water
addition. The salt loop was operated to maintain a
conductivity of 40-50 millisiemens/centimeter (ms/cm) though
10   the continuous addition of the 25 wt% sodium hypophosphite
feed solution.

           The hypophosphorous acid loop was operated in a batch
configuration without water addition. Hypophosphorous acid
(0.5 N) was used to initially inventory the cell. Product
15   was periodically removed from the acid recirculation loop to
reduce the product liquor inventory.

           This experiment operated for a total of about 450
minutes. During that time, a total of approximately 1100 ml
of 2.2 N hypophosphorous acid product was obtained including
20   about 600 ml of 2 N acid removed during the operation of the
cell and about 510 ml of 2.5 N acid remaining in the acid
recirculation loop. The concentration of sodium in the
product acid was measured to be 900 and 1080 ppm,
respectively. The concentration of the depleted salt was
25   about 0.8 molar (50 ms/cm). The potential across the cell
was found to be about 1.8 volts/unit cell. The information
in the attached tables details this experimental run.

TABLE 1
EXAMPLE 3 - ACID LOOP

Time (Min.)	H_3PO_2 Normality (Eq/L)	Volume (ml)	Cumulative Acid Current Efficiency (%)	Current Efficiency Per Sampling Period (%)	Avg. $[H_3PO_2]$ for Sample Period (N)
0	0.5	800			
78	0.95	852	84	84.42	0.725
187	1.485	935	85	85.44	1.2175
234	1.66	965	83	73.03	?.5725
234	1.66	865*			
297	1.93	909	82	81.30	1.795
297	1.93	809*			
368	2.2	861	81	75.39	2.065
368	2.2	661*			
420	2.4	696	79	66.87	2.3
420	2.4	496*			
450	2.525	513	78	56.25	2.4625

* Solution removed from the Acid Recirculation Loop

TABLE 2
EXAMPLE 3 - BASE LOOP

Interval (Min.)	NaOH Normality (Eq/L)	Flow Rate (ml/Min)	Base Current Efficiency (%)	Water Make-up (ml/Min)
178	1.53	3.6	89	3.302
10	1.457	3.65	87	3.306
142	1.425	3.55	81	3.321

TABLE 3
EXAMPLE 3 - SALT LOOP

Feed (ml/Min.)	Depleted Salt (ml/Min)	H3PO2 Normality (Eq/L)	Conductivity (ms/cm)
2.2	0.94	0.23	41.5
2.259	1.091	0.21	48.5

The cumulative current efficiencies (CE) shown in Table 1 show that 2.2 N hypophosphorous acid can be generated on a batch basis. This is significantly higher than the 1 N concentration and 80% CE reported in the open literature for strong acids (Mani, 1991). Table 1 also shows that if current efficiencies are calculated for each discrete sampling period, the concentration of hypophosphorous acid can be expected to be about 1.87 at 80% CE (see Figure 3, line A). As the Figure 3 indicates, this CE is lower than the cumulative efficiency since the early part of the batch cycle operates at high current efficiency when the hypophosphorous acid concentration is relatively low. This data provides some insight as to how a cell operating in a continuous bleed and feed mode would operate at a given current efficiency. For example, a 56% CE would be predicted for a cell operating at 2.5 N H_3PO_2.

The sodium concentration in the 600 ml of 2.0 normal product hypophosphorous acid collected during the experimental run was found to be 900 ppm, while that of the residual product liquor in the acid recirculation loop was 1080 ppm. These concentrations are slightly lower than those reported as being typical by Mani, 1991, at equivalent acid and base concentrations. The base normality was 1.32. Table 4 summarizes the experimental results for this example and Examples 4 and 5 and compares the results to those predicted in Mani, 1991.

TABLE 4
Acid Loop
Sodium Contamination

Acid Nor.	Mole% Na 100% HPA Basis	Wt% HPA	Dens. g/cc	% Na As-is	Source
2.00	2.05	12.30	1.100	0.0897	Actual - Example 3
2.50	2.01	15.10	1.116	0.1077	Actual - Example 3
5.70	2.65	33.33	1.180	0.3156	Actual - Example 4
5.70	4.42	33.33	1.180	0.5370	Actual - Example 5
1.00	2.5	6.75	1.081	0.0379	Predicted, Mani 1991

The table shows that at 2.0 normal hypophosphorous acid, the actual product contamination was about 2.0 mole% sodium vs. 2.5 mole% predicted by Mani, 1991.

Example 4

This example demonstrates the continuous mode of operation for a bipolar membrane cell and supports the conclusion expressed in Example 3 that concentrations of hypophosphorous acid significantly higher than 1 N are possible at a given current efficiency during the electrodialytic splitting of sodium hypophosphite salt into its acid and base components using a three-compartment cell equipped with anion, cation, and bipolar membranes.

In this test, the salt and base streams were operated in a continuous bleed and feed mode. The base loop caustic concentration was maintained at about 5 wt% NaOH with water addition. The salt loop was operated to maintain a

5   conductivity of 70 ms/cm through the continuous addition of the 25 wt% sodium hypophosphite feed solution.

The hypophosphorous acid loop was operated in a continuous configuration without water addition. In this mode of operation, product was allowed to continuously

10   overflow the hypophosphorous acid recirculation loop into a product collection vessel. Hypophosphorous acid (5.0 N) was used to initially inventory the cell.

This experiment operated for a total of about 430 minutes. During that time, a total of approximately 210 ml

15   of 5.7 N hypophosphorous acid product was obtained. The concentration of sodium in the product acid was measured to be 3156 ppm. The concentration of hypophosphorous acid approached 6 N on a steady state basis. The depleted salt concentration was about 0.9 molar $NaH_2PO_2 \cdot H_2O$. The potential

20   across the cell was found to be about 1.8 volts/unit cell. The information in the attached tables details this experimental run.

25

30

TABLE 5
EXAMPLE 4 - ACID LOOP

Time Interval (Min.)	Cumulative Time (Min.)	[H$_3$PO$_2$] (M)	Acid Flow Rate (ml/Min.)	Current Efficiency (%)
97	97	5.45	0.535	46.89
60	157	5.7	0.517	47.40
45	202	5.75	0.52	48.09
46	248	5.8	0.509	47.48
54	302	5.85	0.518	48.74
54	356	6	0.511	49.31
40	396	6	0.525	50.66

TABLE 6
EXAMPLE 4 - BASE LOOP

Time Interval (Min)	Cumulative Time (Min)	[NaOH] (M)	Base Flow Rate (ml/Min)	Water Make-up (ml/Min.)	Caustic Current Efficiency (%)
101	101	1.375	3.47	3.29	76.74
114	215	1.4	3.036	2.89	68.36
102	317	1.495	2.894	2.71	69.59
97	414	1.52	2.771	2.7	67.74

TABLE 7
EXAMPLE 4 - SALT LOOP

Time Interval (Min.)	Cumulative Time (Min.)	Feed Rate (ml/Min.)	Depleted Salt Flow Rate	[H$_3$PO$_2$] (M)
97	97	2.17	1.38	0.47
121	218	2.34	1.44	0.64
208	426	2.35	1.44	0.68

The acid product data in Table 5 shows that a current efficiency of 51% is possible at a hypophosphorous acid concentration of 6 molar. Contrasting this information with the batch operation described in Example 3, Table 1, it can

5   be seen that at 2.5 molar, the current efficiency per sampling period is about 56%. These two drastically different hypophosphorous acid concentrations at about equivalent current efficiencies provide additional support to the conclusion that acid concentrations significantly

10   higher than those reported in the open literature for strong acids are possible during the bipolar membrane electrodialyses of sodium hypophosphite into hypophosphorous acid and sodium hydroxide. The data also indicates that the concentrations attainable in Example 3 at various current

15   efficiencies for sampling periods may in fact be conservative in contrast to what is attainable under continuous operation. Evidenced by the shape of the curve for the batch/semi-batch data (see Figure 3, line B), the nearly 6 molar acid concentration would not be expected

20   based on the batch/semi-batch data.

The concentration of sodium in the hypophosphorous acid was measured in a 5.7 molar composite sample collected during the run. The analyses showed the sample contained 3156 ppm Na. Table 4 compares this result to those of

25   Example 3. The result on a mole percent basis is about that predicted by Mani, 1991 for 1 molar acid vs the 5.7 molar acid generated in this example.

Example 5

This example demonstrates the continuous mode of operation for a bipolar membrane cell and supports the conclusion expressed in Example 3 that concentrations of

5   hypophosphorous acid significantly higher than 1 N are possible at a given current efficiency during the electrodialytic splitting of sodium hypophosphite salt into its acid and base components using a three-compartment cell equipped with anion, cation, and bipolar membranes.

10   In this test, the salt and base streams were operated in a continuous bleed and feed mode. The base loop caustic concentration was maintained at about 5 wt% NaOH with water addition. The salt loop was operated to maintain a conductivity of 70 ms/cm through the continuous addition of

15   the 25 wt% sodium hypophosphite feed solution.

The hypophosphorous acid loop was operated in a continuous configuration without water addition. In this mode of operation, product was allowed to continuously overflow the hypophosphorous acid recirculation loop into a

20   product collection vessel. Hypophosphorous acid (5.0 N) was used to initially inventory the cell.

This experiment operated for a total of about 450 minutes. During that time, a total of approximately 240 ml of 5.7 N hypophosphorous acid product was obtained. The

25   concentration of sodium in the product acid was measured to be 5370 ppm. The concentration of hypophosphorous acid approached 5.8 N on a steady state basis. The depleted salt concentration was about 0.85 molar $NaH_2PO_2 \cdot H_2O$. The

potential across the cell was found to be about 1.8

volts/unit cell. The information in the attached tables

details this experimental run.

TABLE 8
EXAMPLE 5 - ACID LOOP

Time Interval (Min.)	Cumulative Time (Min.)	[H_3PO_2] (M)	Acid Flow Rate (ml/Min.)	Current Efficiency (%)
81	81	5.1	0.47	38.55
71	152	5.35	0.55	47.33
45	197	5.45	0.56	49.09
90	287	5.8	0.54	50.37
92	379	5.8	0.54	50.37

TABLE 9
EXAMPLE 5 - BASE LOOP

Time Interval (Min.)	Cumulative Time (Min.)	[NaOH] (M)	Base Flow Rate ml/Min	Water Make-up ml/Min	Current Effi-ciency (%)
95	95	1.32	2.99	2.75	63.48
37	132	1.4	2.84		63.95
20	152	1.26	3.36	2.78	68.09
39	191	1.26	3.26		66.06
140	331	1.26			
36	367	1.56	3.1	2.78	77.78

TABLE 10
EXAMPLE 5 - SALT LOOP

Time Interval (Min.)	Cumulative Time (Min.)	Feed Rate (ml/Min.)	Depleted Salt Flow Rate	[H_3PO_2] (M)
75	75	2.033	1.17	0.79
41	116	2.033	1.17	0.69
85	201	2.033	1.14	0.63
35	236	2.033	1.14	0.64

The acid product data in Table 5 shows that a current efficiency of 50% is possible at a hypophosphorous acid concentration of 5.8 molar. Again, contrasting this information with the batch operation described in Example 3,

5   Table 1, it can be seen that at 2.5 molar, the current efficiency per sampling period is about 56%. The difference in hypophosphorous acid concentrations at about equivalent current efficiencies, as in Example 4, supports the conclusion that acid concentrations significantly higher

10   than those reported in the open literature for strong acids are possible during the bipolar membrane electrodialyses of sodium hypophosphite into hypophosphorous acid and sodium hydroxide. A comparison of Example 4 with Example 5 shows that the concentration and current efficiency results are

15   reproducible. The data also indicates that the concentrations attainable in Example 3 at various current efficiencies for sampling periods may in fact be conservative in contrast to what is attainable under continuous operation. Evidenced by the shape of the curve

20   for the batch/semi-batch data (see Figure 3, line C), the nearly 5.8 molar acid concentration would not be expected based on the batch/semi-batch data.

The concentration of sodium in the hypophosphorous acid was measured in a 5.7 molar composite sample collected

25   during the run. The analyses showed the sample contained 5170 ppm Na. Table 4 compares this result to those of Examples 3 and 4. The result on a mole percent basis is higher than that predicted by Mani, 1991.

WE CLAIM

1.   A method of making hypophosphorous acid and sodium
       hydroxide from sodium hypophosphite comprising
       performing electrodialytic water splitting upon an
       aqueous solution of said sodium hypophosphite.

2.   A method according to Claim 1 wherein said
       electrodialytic water splitting is performed in an
       electrolytic cell having the structure
       Anode-A-AM-[S-CM-B-BM-A-AM]$_n$-S-CM-B-Cathode
       where CM is a cationic exchange membrane, B is a base
       compartment containing an aqueous solution of sodium
       hydroxide product, BM is a bipolar ion exchange
       membrane, A is an acid compartment containing an
       aqueous solution of hypophosphorous acid product, AM is
       an anion exchange membrane, S is a salt compartment
       containing an aqueous solution of sodium hypophosphite,
       and n is 1 to 200.

3.   A method according to Claim 1 wherein said
       electrodialytic water splitting is performed in an
       electrolytic cell having the structure
       Anode-ER-CM-B-BM-A-AM-[S-CM-B-BM-A-AM]$_n$-
            S-CM-B-CM-ER-Cathode

where CM is a cationic exchange membrane, B is a base
compartment containing an aqueous solution of sodium
hydroxide product, BM is a bipolar ion exchange
membrane, A is an acid compartment containing an
aqueous solution of hypophosphorous acid product, AM is
an anion exchange membrane, S is a salt compartment
containing an aqueous solution of sodium hypophosphite,
ER is an electrode rinse compartment, and n is 1 to
200.

4.   A method according to Claim 1 wherein said
      electrodialytic water splitting is performed in an
      electrolytic cell comprising

      (1)   an anode electrode rinse compartment housing an
            anode;

      (2)   a cathode electrode rinse compartment housing a
            cathode;

      (3)   a series of at least two juxtaposed units in
            between said anode electrode rinse compartment and
            said cathode electrode rinse compartment, where
            each unit comprises

            (a)   a base compartment containing an aqueous
                  solution of sodium hydroxide product;

            (b)   an acid compartment containing an aqueous
                  solution of hypophosphorous acid product;

            (c)   a salt compartment containing an aqueous
                  solution of sodium hypophosphite and
                  hypophosphorous acid;

(d) a bipolar ion exchange membrane between each base compartment and adjacent acid compartment; and

(e) an anion exchange membrane between each acid compartment and adjacent salt compartment, where the salt compartment of one unit is separated from the base compartment of the adjacent unit by a cation exchange membrane and the base compartment at one end of said series is adjacent said anode electrode rinse compartment and the base compartment at the opposite end of said series is adjacent said cathode electrode rinse compartment;

(4) means for circulating said aqueous solution of sodium hydroxide product through said base compartments;

(5) means for circulating said aqueous solution of sodium hypophosphite and hypophosphorous acid through said salt compartments;

(6) means for circulating said aqueous solution of hypophosphorous acid through said acid compartments;

(7) means for circulating aqueous electrode rinse solutions through said electrode rinse compartments;

(8) means for adding water to said acid compartment;

(9) means of adding water to said base compartment; and

(10) means of adding an aqueous solution of sodium
     hypophosphite to said salt compartment.

5.   A method according to Claim 4 wherein an additional
      cation exchange membrane is placed at each end of said
      series of units to form said electrode rinse
      compartments.

6.   A method according to Claim 4 wherein the concentration
      of said aqueous solution of sodium hypophosphite is
      about 5 to about saturation.

7.   A method according to Claim 4 wherein the concentration
      of said aqueous solution of sodium hypophosphite and
      hypophosphorous acid in the salt compartment is about 1
      to 50 wt% and 0 to 55 wt%, respectively.

8.   A method according to Claim 4 wherein the temperature
      of said cell is about 10 to about 45°C.

9.   A method according to Claim 4 wherein the current
      density in said cell is about 50 to about 155 mA/cm^2.

10.   A method according to Claim 4 wherein the linear
      solution velocities of said aqueous solutions through
      said cell are about 2 to about 15 cm/sec.

11.   A method according to Claim 4 wherein a portion of said hypophosphorous acid and sodium hydroxide solutions is continuously drawn off and replaced with water and a portion of said sodium hypophosphite and hypophosphorous acid solution is continuously drawn off and replaced with fresh sodium hypophosphite solution.

12.   A method according to Claim 4 wherein, whenever a predetermined concentration of hypophosphorous acid is reached in said hypophosphorous acid solution, a portion of said hypophosphorous acid solution is drawn off.

13.   A method according to Claim 4 wherein the concentration of sodium hydroxide in said sodium hydroxide solution is maintained at less than 10 wt%.

14.   A method according to Claim 4 wherein the pressure in the acid compartments is about 1 to about 3 psi greater than the pressure in the base and salt compartments.

15.   A method according to Claim 4 including the additional last step of using at least a portion of said sodium hypophosphite and hypophosphorous acid solution to adjust the pH of a second aqueous sodium hypophosphite solution prior to the evaporation and crystallization of said second aqueous sodium hypophosphite solution.

16. A method according to Claim 15 wherein the concentration of said hypophosphorous acid in said hypophosphorous acid solution and the concentration of said sodium hydroxide in said sodium hydroxide solution are controlled so that the acid content of said sodium hypophosphite and hypophosphorous acid solution is the content needed to reduce the pH of said second aqueous sodium hypophosphite solution to the desired pH.

17. A method according to Claim 4 including the additional last step of passing at least a portion of said hypophosphorous acid solution through cation exchange material loaded with hydrogen ions to replace sodium ions that may be present in said solution with hydrogen ions.

18. A method of making hypophosphorous acid in an electrodialytic water splitter cell having about 1 to about 200 juxtaposed units, where said cell comprises

(1) an anode electrode rinse compartment housing an anode;

(2) a cathode electrode rinse compartment housing a cathode;

(3) a series of at least two juxtaposed units in between said anode electrode rinse compartment and said cathode electrode rinse compartment, where each unit comprises

(a) a base compartment containing an aqueous solution of sodium hydroxide product;

(b) an acid compartment containing an aqueous solution of hypophosphorous acid;

(c) a salt compartment containing an aqueous solution of sodium hypophosphite and hypophosphorous acid;

(d) a bipolar ion exchange membrane between each base compartment and adjacent acid compartment; and

(e) an anion exchange membrane between each acid compartment and adjacent salt compartment,

where the salt compartment of one unit is separated from the base compartment of the adjacent unit by a cation exchange membrane and the base compartment at one end of said series is adjacent the anode electrode rinse compartment and the salt compartment at the opposite end of said series is adjacent the cathode electrode rinse compartment;

(4) means for circulating said aqueous solution of sodium hydroxide product through said base compartments;

(5) means for circulating said aqueous solution of sodium hypophosphite and hypophosphorous acid through said salt compartments; and

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(6) means for circulating said aqueous solution of
     hypophosphorous acid through said acid
     compartments;

(7) means of circulating aqueous electrode rinse
     solutions through said electrode rinse
     compartments;

(A) adding water to said acid and base compartments;

(B) adding an aqueous solution of about 5 to about
     saturation of sodium hypophosphite to said salt
     compartments;

(C) maintaining the temperature in said series of
     units at about 10 to about 45°C;

(D) passing direct current through said series of
     units at a density of about 50 to about 155
     mA/cm², whereby said sodium hypophosphite and
     water react in said cell to produce an aqueous
     solution of hypophosphorous acid in said acid
     compartments and an aqueous solution of sodium
     hydroxide in said base compartments;

(E) maintaining the concentration of sodium hydroxide
     in said base compartments at less than about 10
     wt% by replacing at least a portion of said sodium
     hydroxide solution with water;

(F)   maintaining the concentration of sodium hypophosphite in said salt compartments at about 5 to about saturation by drawing off depleted sodium hypophosphite solution from said salt compartments and replacing said drawn off solution with fresh aqueous sodium hypophosphite solution having a concentration of about 5 to about saturation;

(G)   removing hypophosphorous acid solution from said acid compartments and replacing said removed hypophosphorous acid solution with water; and

(H)   maintaining the pressure in the acid compartment at about 1 to about 3 psi greater than the pressure in the base and salt compartments.

19.   A method according to Claim 18 wherein a portion of said hypophosphorous acid solution is removed from said acid compartments and is replaced with water whenever the concentration of hypophosphorous acid in said compartments reaches about 10 to about 55 wt%.

20.   A method according to Claim 19 wherein a portion of said hypophosphorous acid solution is continuously removed from said acid compartments and is continuously replaced with water in order to maintain the concentration of hypophosphorous acid in said compartments below a concentration between about 10 and about 30 wt%.

21. A method according to Claim 18 wherein a portion of said hypophosphorous acid solution is continuously removed from said acid compartments without replacement with water in order to obtain the maximum concentration of hypophosphorous acid possible in said compartments.

22. A method according to Claim 18 wherein the concentration of hypophosphorous acid in said salt compartments is maintained at about 0 to about 55 wt% by drawing off depleted salt solution from said salt compartments and replacing it with about 0 to about 55 wt% aqueous sodium hypophosphite solution.

23. In a process for making sodium hypophosphite wherein the pH of a sodium hypophosphite aqueous liquor is lowered with an acid other than hypophosphorous acid prior to evaporative crystallization of sodium hypophosphite, a method of producing hypophosphorous acid from at least a portion of the sodium hypophosphite thereby produced, comprising

    (a) performing electrodialytic water splitting upon an aqueous solution of at least a portion of said sodium hypophosphite to produce said hypophosphorous acid and a depleted sodium hypophosphite solution containing hypophosphorous acid; and

    (b) replacing said other acid with at least a portion of said depleted sodium hypophosphite solution.
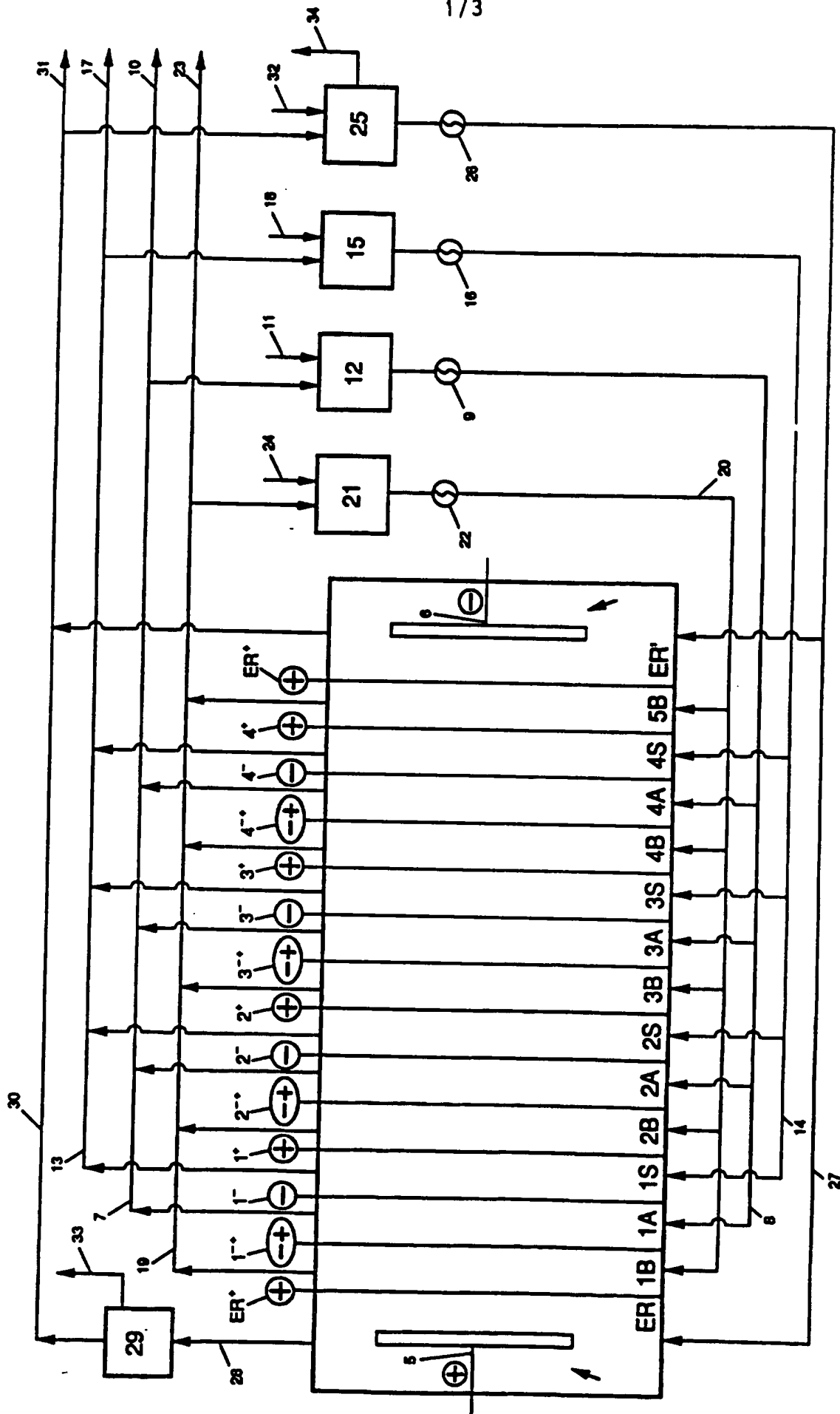
Figure 1
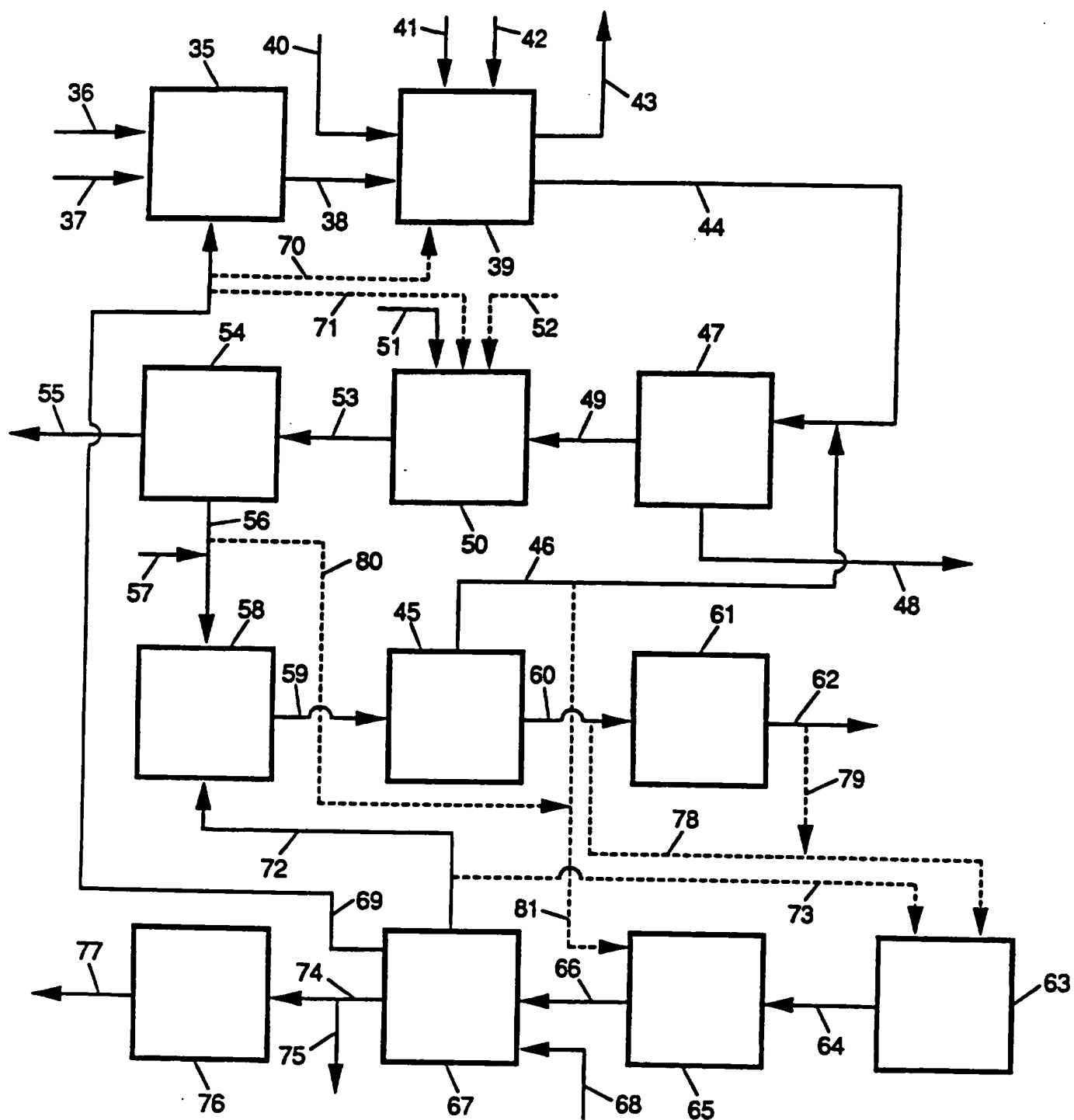
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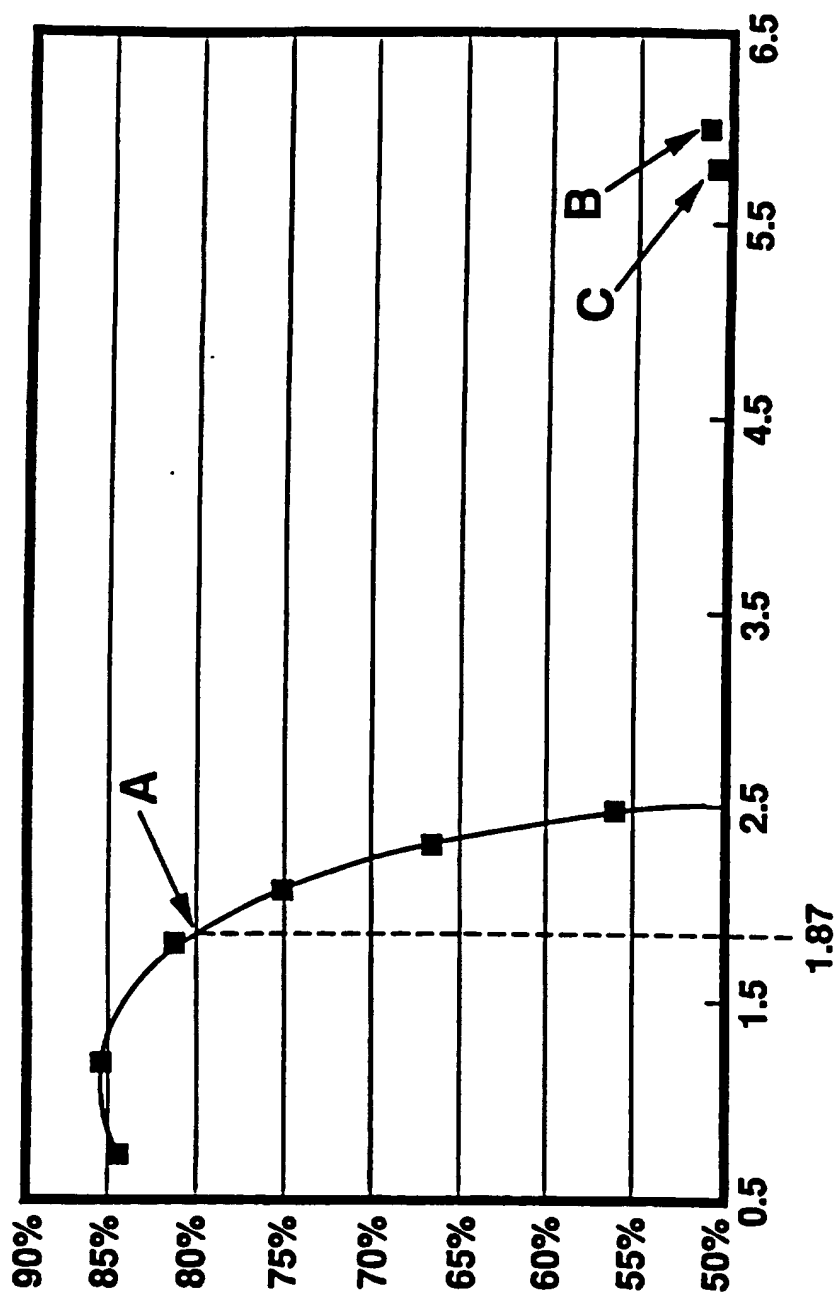
Figure 3

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6   C01B25/165   B01D61/44

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6   C01B   B01D   C25B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT		
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☐ Further documents are listed in the continuation of box C.	☒ Patent family members are listed in annex.

Date of the actual completion of the international search	Date of mailing of the international search report
3 July 1995	12.07.95

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016	Devisme, F

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